

# **HIGH ENERGY AND LONG-LIFE LITHIUM-SULFUR CELLS**

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**And**

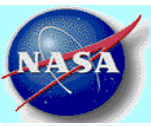
**Mary Hendrickson and Ed Plichta**

**US Army RDECOM CERDEC CP&I, Aberdeen Proving Ground, MD 21005**

**Li-SM<sup>3</sup> 2017 conference**

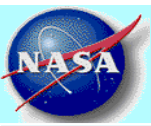
**IET Savoy Place, London**

**April 26, 2017**



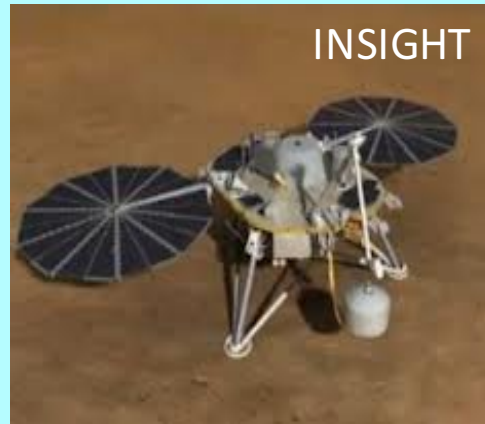
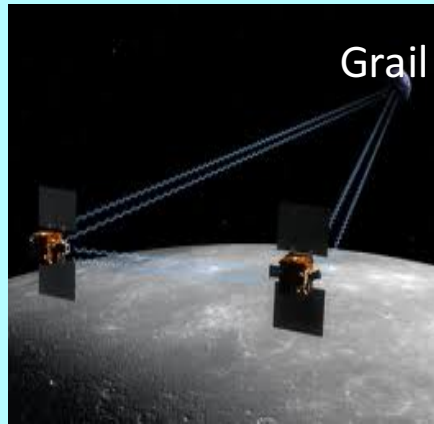
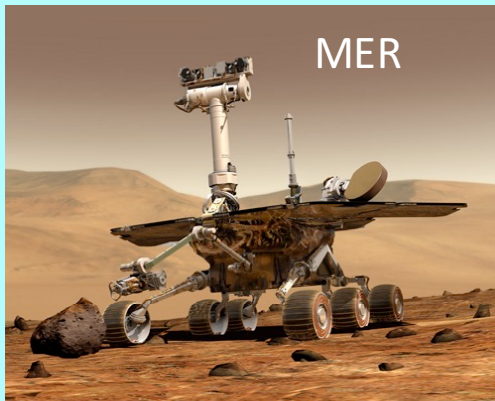
# Batteries for Space Applications

| Category  | Mission                | Battery Performance Drivers  | Chemistry                                     |
|---|------------------------|--|---|
| Outer Planets: Ocean Worlds (Europa, Titan, Enceladus)    | Orbital Missions       | Long Cycle life (at partial depth of discharge)                      | Li-ion  |
|   | Surface Missions       | Primary or rechargeable - high specific energy, long calendar life   | Li-CF <sub>x</sub> or Li-ion,                 |
|   | Sample Return Missions | Primary Long calendar life High specific energy and energy density   | Li-CF <sub>x</sub> and Li-SOCl <sub>2</sub> , |
| Outer Planets: ICE Giants (Neptune, Uranus)               | Orbiters               | Long Cycle life (at partial depth of discharge)                      | Li-ion  |
|   | Probes                 | Primary - high specific energy, long calendar life                   | Li-CF <sub>x</sub> and Li-SOCl <sub>2</sub> , |
| Inner Planets: Venus                                      | Orbital                | Long Cycle life (at partial depth of discharge)                      | Li-ion  |
|   | Aerial                 | High Temperature, high specific energy and good cycle life           | Na-MCl <sub>2</sub>                           |
|   | Surface                | Primary High Temperature, high specific energy                       | Li-FeS <sub>2</sub>                           |
| Mars  | Sample Return Missions | Primary Long calendar life High specific energy and energy density   | Li-CF <sub>x</sub> and Li-SOCl <sub>2</sub> , |
|   | Orbital Missions       | Long Cycle life (at partial depth of discharge)                      | Li-ion  |
|   | Aerial Missions        | High specific energy, energy density and high power density          | Li-ion  |
|   | Surface Missions       | High specific energy, energy density and low temperature performance | Li-ion  |
| Small Bodies : Multi-asteroid rendezvous or flyby mission | Sample Return Missions | Primary Long calendar life High specific energy and energy density   | Li-SO <sub>2</sub> Li-SOCl <sub>2</sub> ,     |
|   | Surface missions       | Primary or rechargeable - high specific energy,                      | Li-ion or Li-S                                |
| Planetary Cube Sat/ Small Spacecraft                      |                        | High specific energy, energy density and low temperature performance | Li-ion or Li-S                                |
| Interstellar Missions                                     |                        | Long Calendar life   | Li-Solid State?                               |



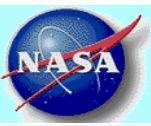
# LI-Ion Batteries in Space Missions

## Missions using batteries with Large format Cells



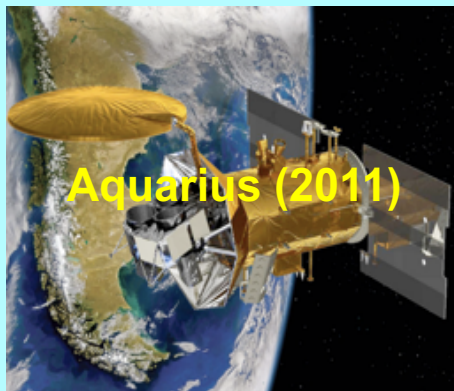
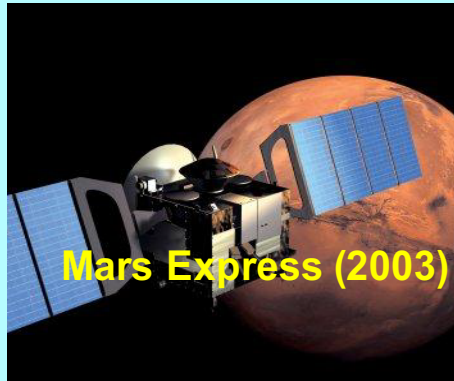
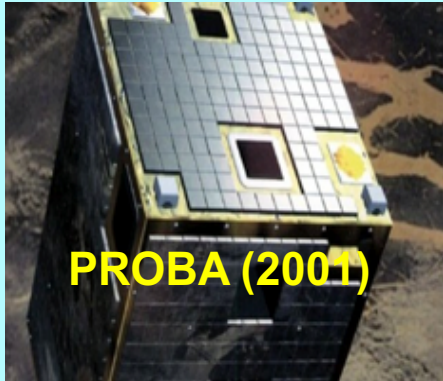
- Custom prismatic cells from 10-135 Ah
- Chemistry (MCMB anode,  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode and low temperature electrolyte)
- Space station cells with graphite anode,  $\text{LiNi}_{0.8}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2$  cathode
- Cylindrical cells (SAFT) in several satellites





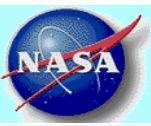
# LI-Ion Batteries in Space Missions

## Missions with small Commercial Cells



- Commercial 18650 cells originally from Sony (hard carbon–LiCoO<sub>2</sub>).
- Recent batteries have cells with high specific energies (>220 Wh/kg)
- No need for cell balancing electronics





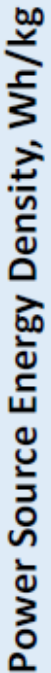
# Application for Li-S Batteries

- **Astronaut EVA Requirements**
  - Eight hours of run time
  - High specific energy of 250 Wh/kg (battery) or 400 Wh/kg (at the cell level )
  - Cycle life 100-200 cycles
  - Evaluated Li-rich NMC cathodes and Si anodes over the last few years. Despite encouraging results in half-cells, the performance in prototype cells wasn't as impressive.
  - Li-S is the system that can possibly meet these requirements, due to the short cycle life requirement.
- **Unmanned aerial vehicles (UAVs) or drones**
- **Planetary rovers**
- **Army applications (soldier power)**

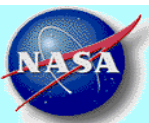


**Portable Life Support System**

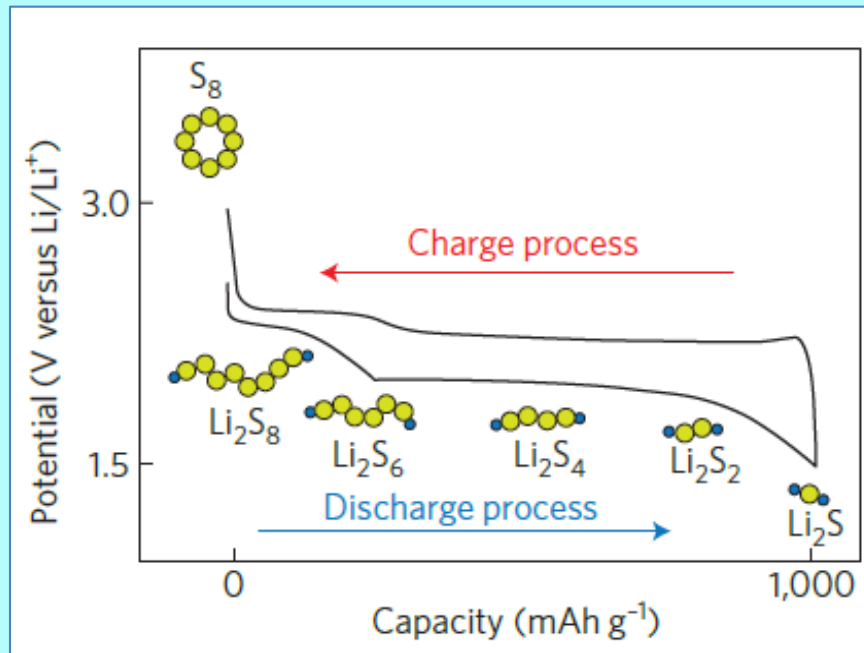
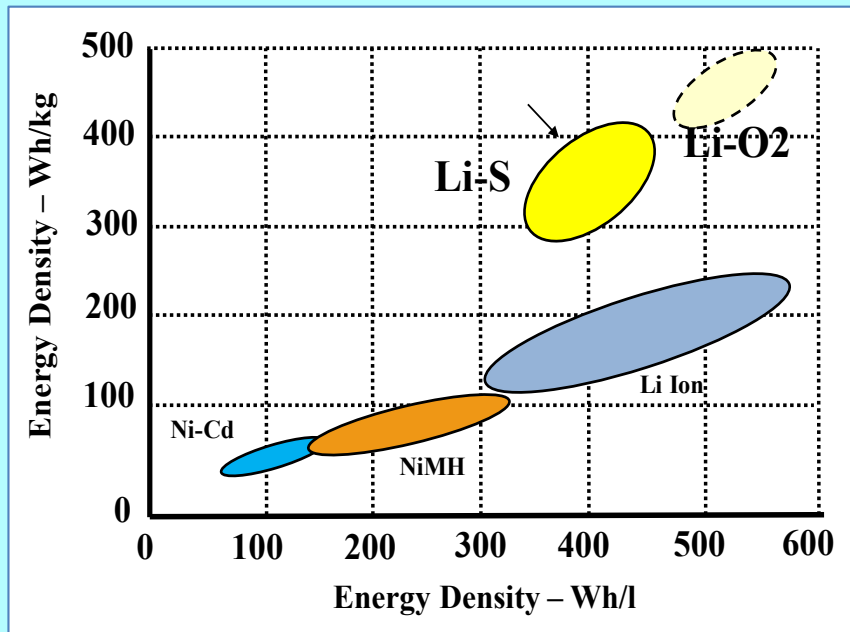




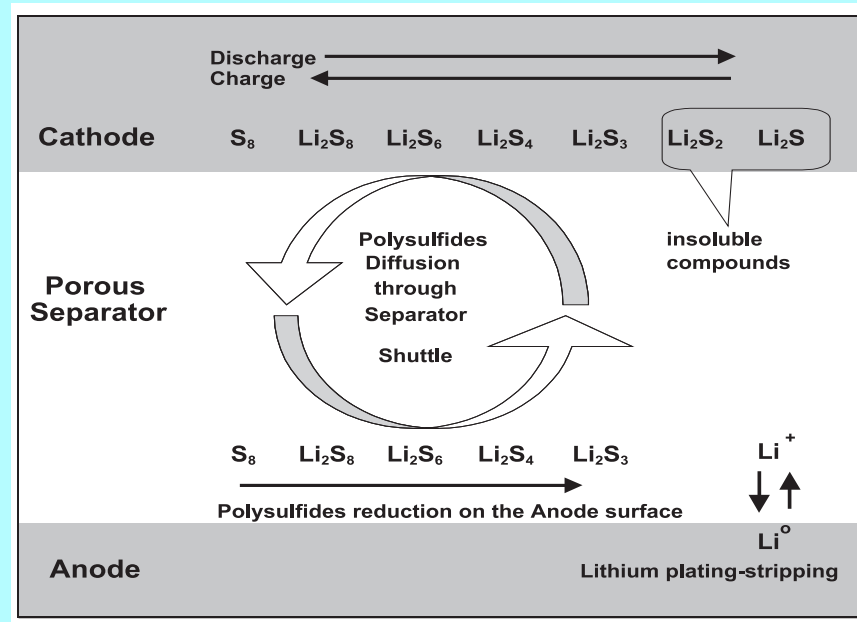
- Li-SM<sup>3</sup> 2017 conference, London, April 26-27, 2017*



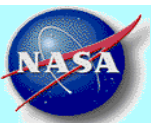
# Why Lithium-Sulfur Batteries



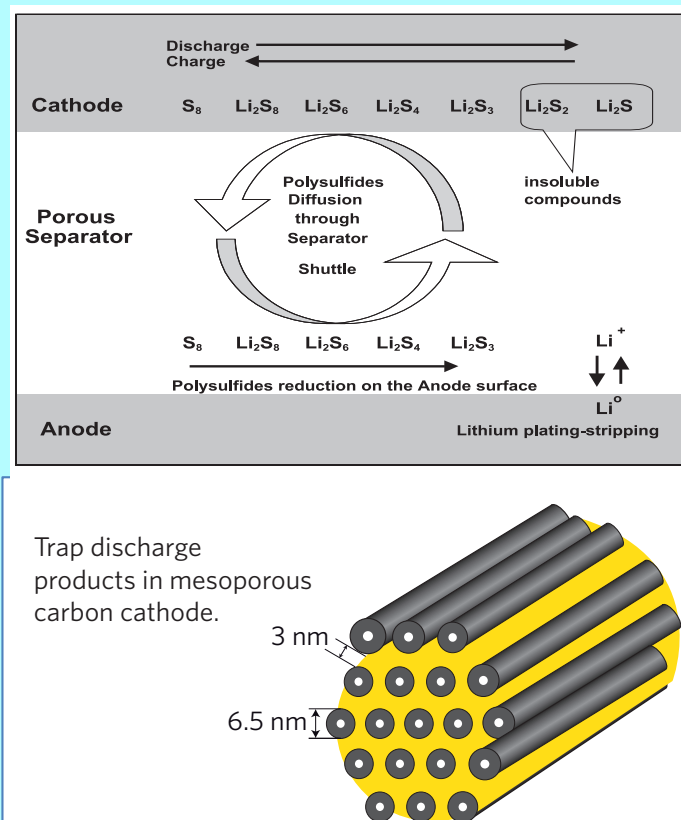
- High specific capacity of 1670  $\text{mAh/g}$ ;
- High theoretical specific energy of 2567  $\text{Wh/kg}$
- Inexpensive and Environmentally benign
- Abundant in the Earth's crust
- 250-400  $\text{Wh/kg}$  realized in practical cells.
  - Higher specific energy cells have shorter cycle life







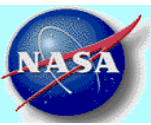
# Problems with Li-S and Mitigation Strategies



- Anode passivation and dendrite formation.
- Sulfur expands by 79%
- Poor conductivity of S and its discharge products.
- Polysulfides are soluble in many solvents : Form Redox shuttle and insulating layer ( $Li_2S$ ) on the anode

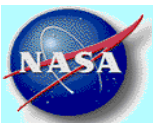
| Problems   | Strategies Adopted   | Rationale  |
|--|--|--|
| Poor cyclability and dendrites                             | Coat with protecting layer (solid electrolyte)                 | Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites                                     |
|  | Coat with protecting layer (gel polymer)                       |  |
| Polysulfide dissolution, redox shuttle behavior            | Immobilize in carbon host matrix                               | Strong S-C interactions trap sulfides (e.g. as $S_n^{x-}$ chain-like species, as cyclo- $S_8$ allotrope does not fit inside pores) |
|  | Use sulfide (discharge product) as cathode                     | Allows use of non-Li anodes  |
| Poor Conductivity and expansion                            | Meso/microporous carbon support for S                          | High electronic conductivity of C mitigates poor S conductivity  |
| Passivation  | Use sulfide (discharge product) as cathode                     | Allows use of non-Li anodes  |
| Soluble sulfides affecting anode stability and performance | Organic electrolyte with additives (e.g. $LiNO_3$ , $P_2S_5$ ) | Good conductivity, additives react preferentially with sulfide species and passivate Li surface, depassivate cathode               |
|  | Ionic liquid electrolyte                                       | Sulfides are insoluble in certain ionic liquids  |
|  | Solid-state electrolyte  | Blocks contact between Li and soluble sulfide species and/or mechanically inhibit Li dendrites                                     |

- Some of these approaches have shown improved cycle life, but only with low sulfur loadings



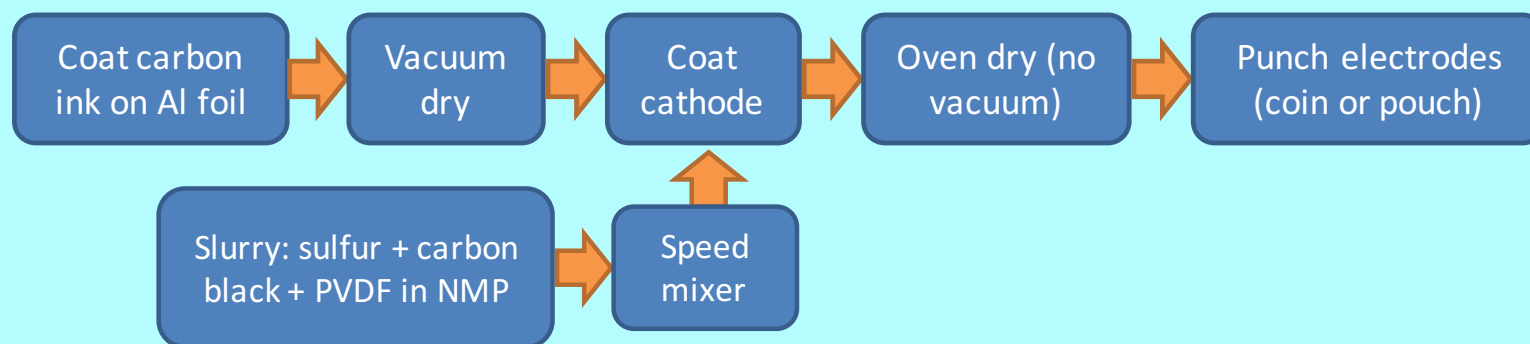
## Sulfur cathode With high Loadings for a 400 Wh/kg Li-S cell

- High cathode loadings required for high energy cells
  - High energy Li-ion cells have cathodes (nickel cobalt aluminum oxide, NCA) with a loading of  $15 \text{ mg/cm}^2$ , i.e.,  $\sim 8.7 \text{ mWh/cm}^2$  per side of the electrode.
  - For a specific energy of 400 Wh/kg, we will need 1.5 times the specific energy compared to Li-ion cells, i.e.,  $13 \text{ mWh/cm}^2$  per side.
  - With a voltage of 2.1 V for Li-S cell, this implies an areal capacity of  $\sim 6.2 \text{ mAh/cm}^2$  for the sulfur cathode.
  - With 800 mAh/g from sulfur (and with a composition of 65% sulfur), the required loading is  $12 \text{ mg/cm}^2$ .
  - Almost all reports of Li-S cells in the literature describe performance of sulfur cathodes with a low loading of  $< 5 \text{ mg/cm}^2$  (mostly  $2\text{-}3 \text{ mg.cm}^{-2}$ ) and/or with low proportion of sulfur in the cathode.

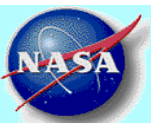


# Electrolytes for Li-S Cells

- Screened different electrolytes with co-solvents and additives:
  - 1.0M LiOTf in DME + DOL (95:5 vol.)
  - 1.0M LiTFSI, DME + DOL (95:5 vol.)
  - 1.0M LiTFSI, DME + DOL (95:5 vol.) + 2% VC
  - 1.0M LiTFSI, DME + TFEB + DOL (75:20:5 vol.) (fluorinated ester co-solvent)
  - 1.0M LiTFSI, DME + FEC + DOL (75:20:5 vol.) (FEC co-solvent)
  - 1.0M LiTFSI, DME+BMP-TFSI+DOL (45:50:5 vol.) – (Ionic Liquid co-solvent)
- Best performance was observed in 1.0M LiTFSI, DME + DOL (95:5 vol.)
- Further improvement with  $\text{LiNO}_3$  (0.2 M) and with a carbon cloth interlayer (Manthiram et al).
- Cathode: Sulfur blended with carbon (Super P) with PVDF binder (55% sulfur + 40% carbon + 5 % PVDF)

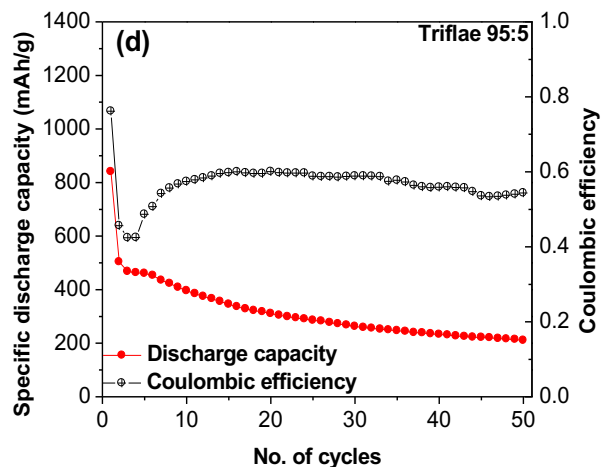




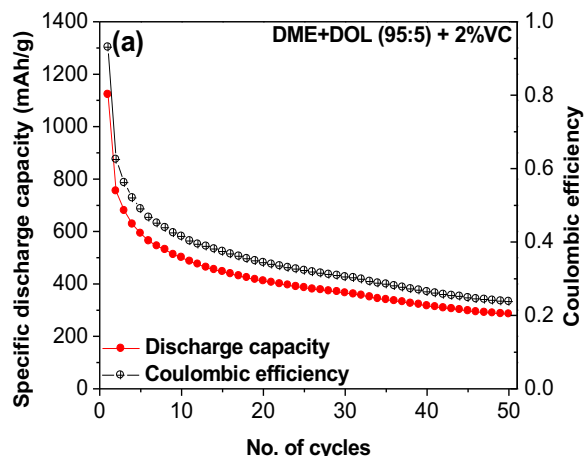


# Effect of Electrolyte in a Li-S Cell

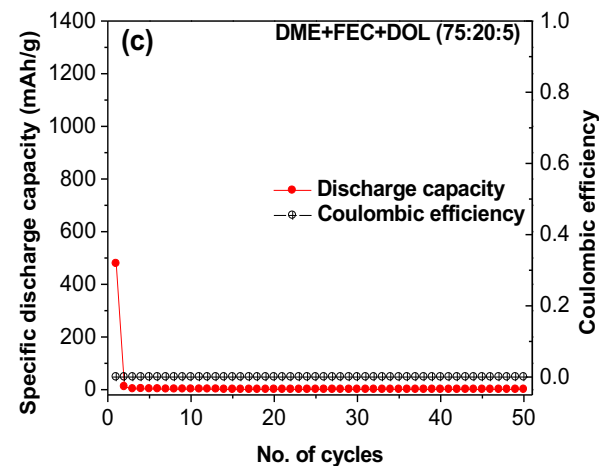
1.0M LiOTf, DME+DOL  
(95:5 vol.)



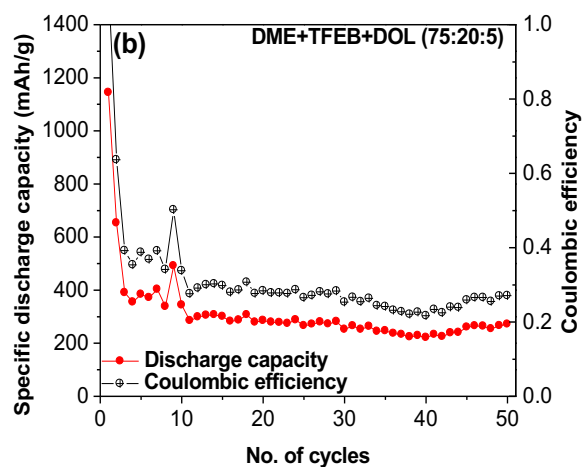
1.0M LiTFSI, DME+DOL (95:5  
vol.) + 2% VC



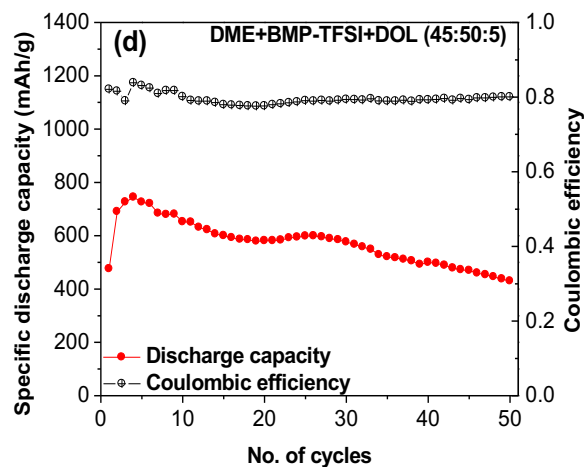
1.0M LiTFSI, DME+FEC+DOL  
(75:20:5 vol.)



1.0M LiTFSI, DME+TFEB+DOL  
(75:20:5 vol.)

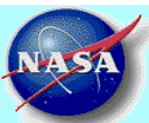


1.0M LiTFSI, DME+BMP-  
TFSI+DOL (45:50:5 vol.)



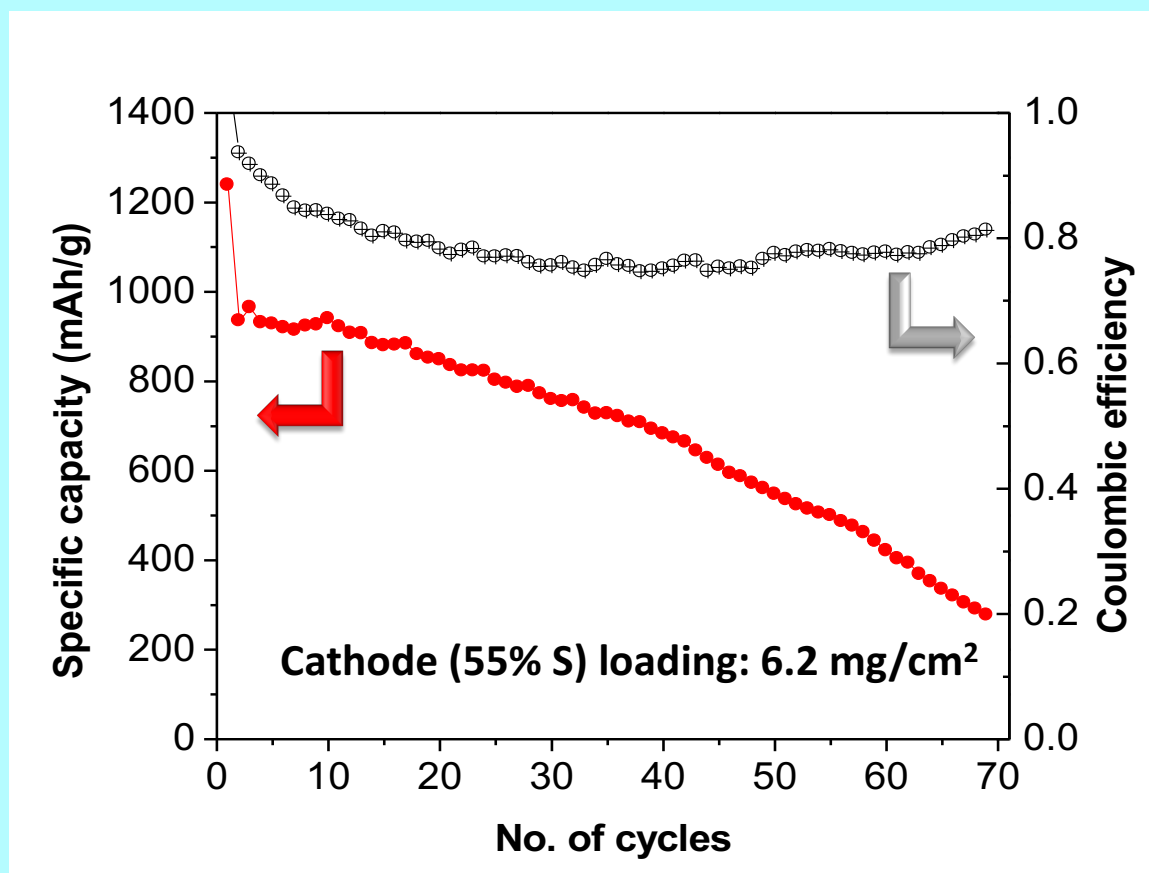
- Imide salt > Triflate salt
- VC additive provides no improvement
- FEC and TFEB co-solvents are not compatible.
- Performance degrades with the ionic liquid (BMP)

Cathode loading: 4-5 mg/cm<sup>2</sup>

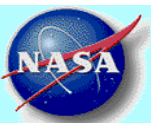


# Sulfur cathode with high Loading in a Li-S cell

1.0M LiTFSI+DME+DOL(95:5) with a Carbon Cloth

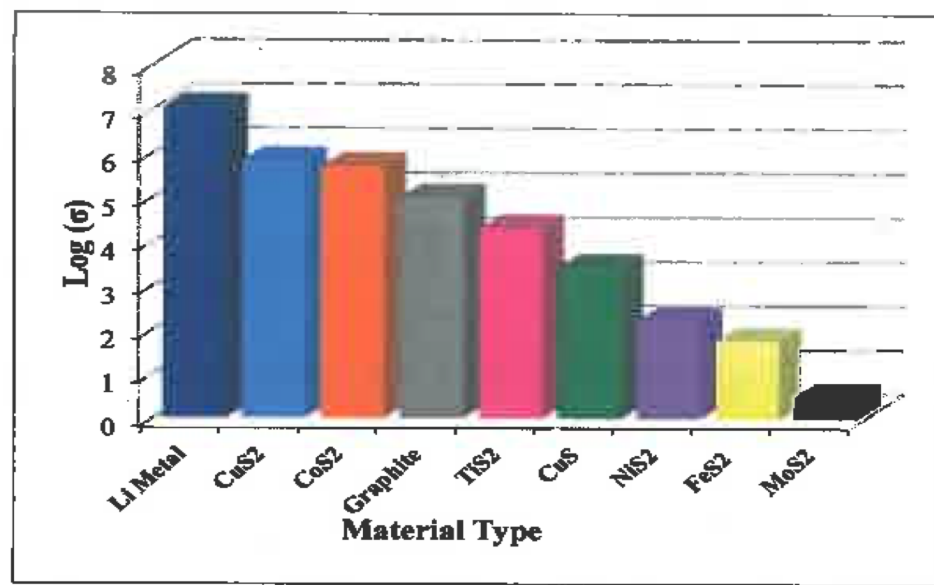


- Lower capacity and utilization of sulfur in thicker cathode even with carbon cloth interlayer and LiNO<sub>3</sub>.
- With a denser sulfur cathodes, more polysulfides are expected to dissolve in the electrolyte.

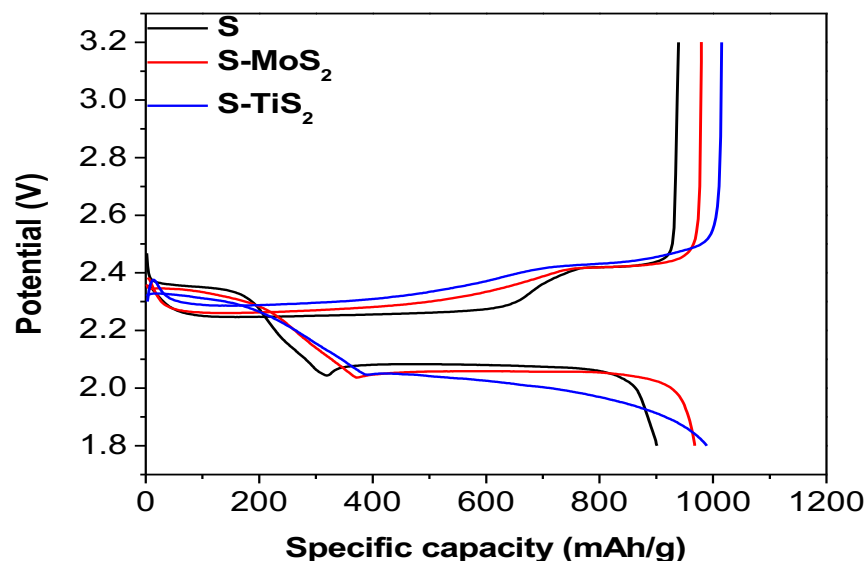


# High Areal Capacity S Cathodes

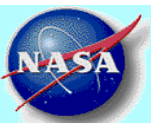
- Transition metal sulfide undergoes reversible reactions around the same voltage range and can add to the cathode capacity and also mediate the sulfur redox reaction.
- Metal sulfide provides some electronic/ionic conductivity can replace portion of the carbon.
  - Easier to make dense electrodes with the metal sulfide additions in place carbon.
- $\text{TiS}_2$  (Manthiram and Cui et al) ,  $\text{VS}_2$ ,  $\text{ZrS}_2$  (Cui et al) with low loadings ( $<5\text{mg/cm}^2$ ),  $\text{CuS}_2$  (Takeuchi et al)
- We Screened several sulfides :  $\text{TiS}_2$ ,  $\text{MoS}_2$  have shown to be beneficial



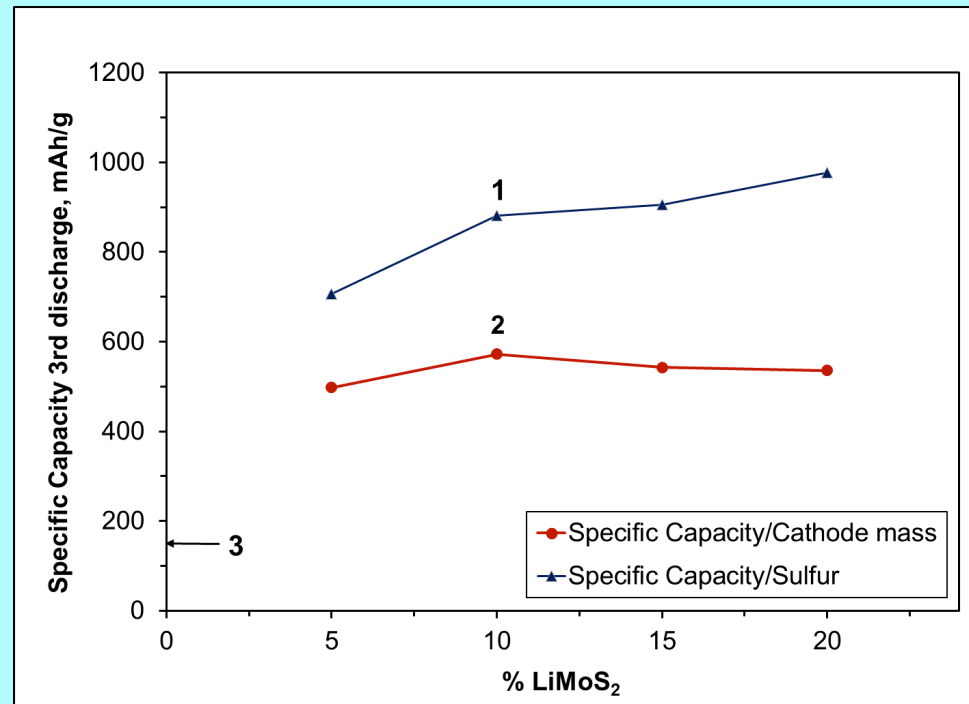
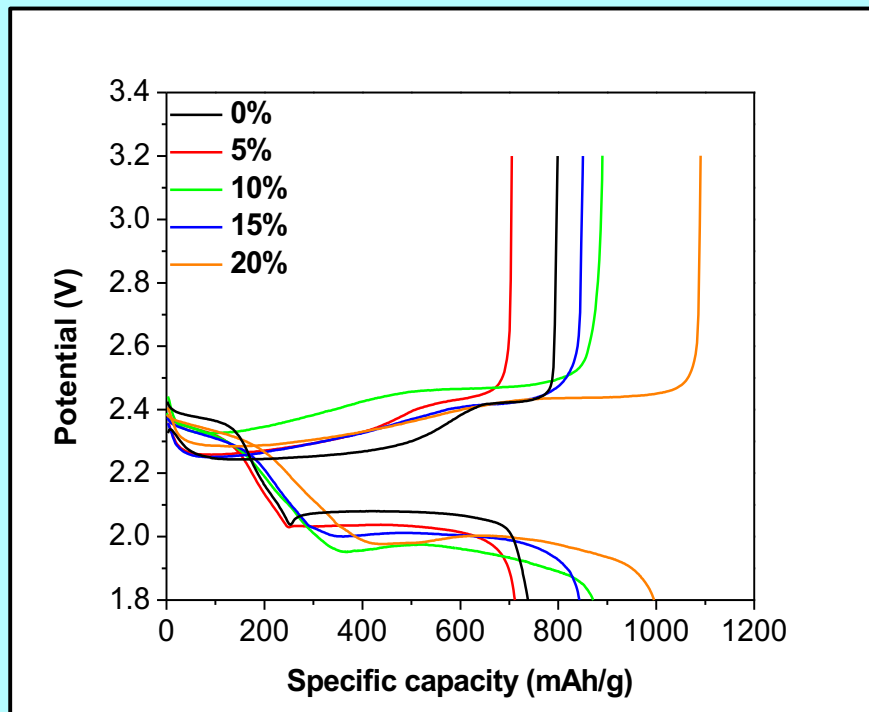
Takeuchi et al DoE Report



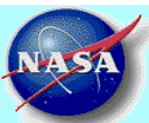




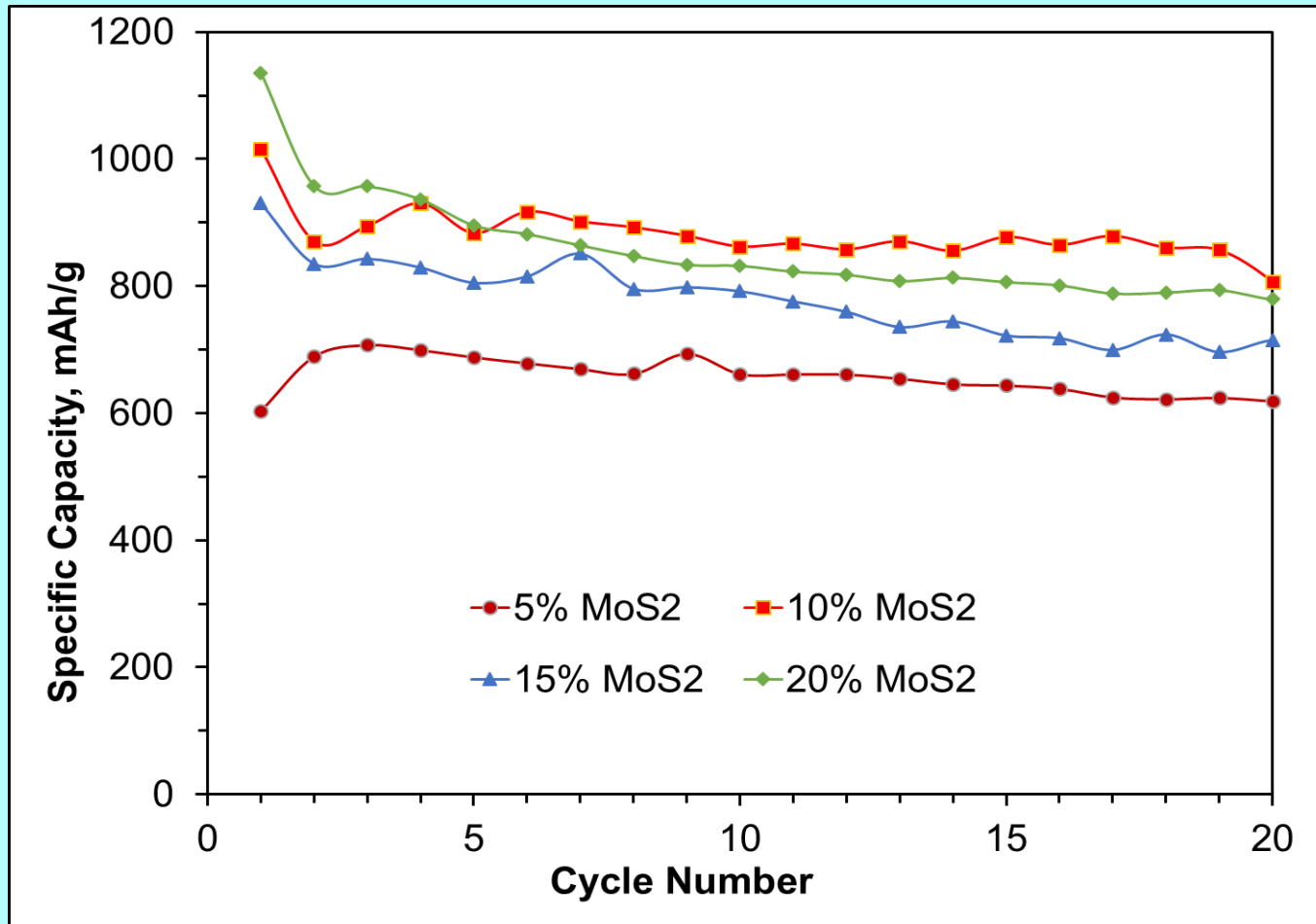
# Sulfur Cathode With Different amounts of $\text{MoS}_2$



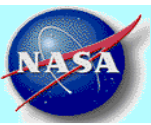
- Three times the capacity per gram of cathode material compared to Li-ion cathode powder (NCA)
- Specific capacity of sulfur increases with  $\text{MoS}_2$  loading, but specific capacity of total cathode does not



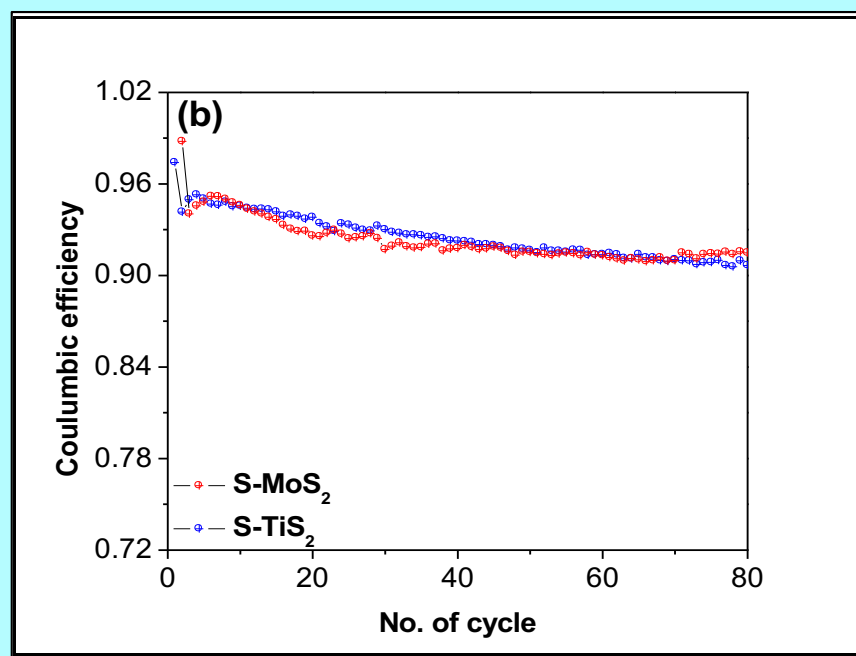
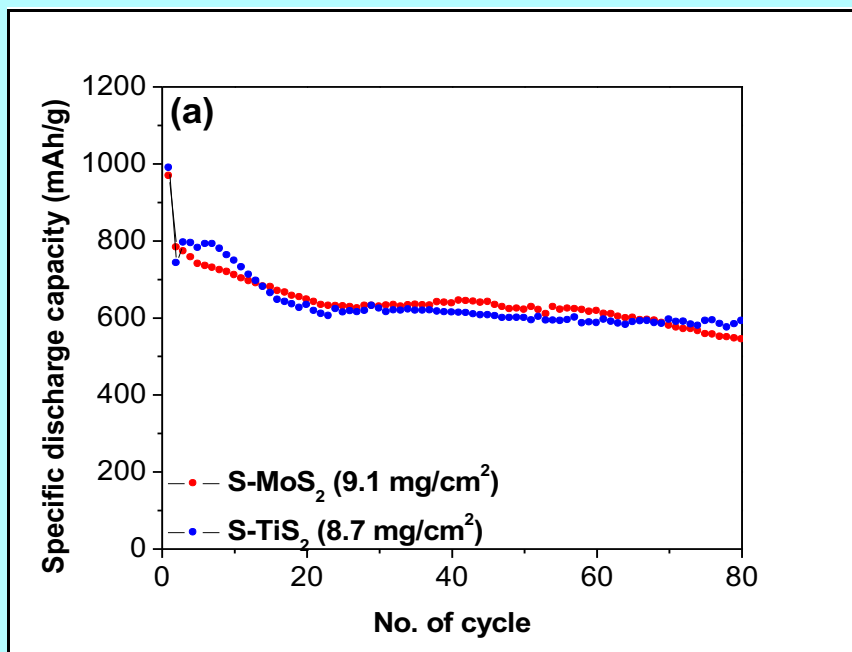
## Sulfur Cathode With Different amounts of MoS<sub>2</sub>



- High sulfur utilization and capacity retention during cycling with 10-15% of MoS<sub>2</sub> in the cathode (65% sulfur)

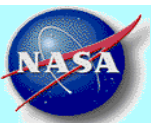


## Sulfur blended with $\text{MoS}_2$ and $\text{TiS}_2$ (15w%)

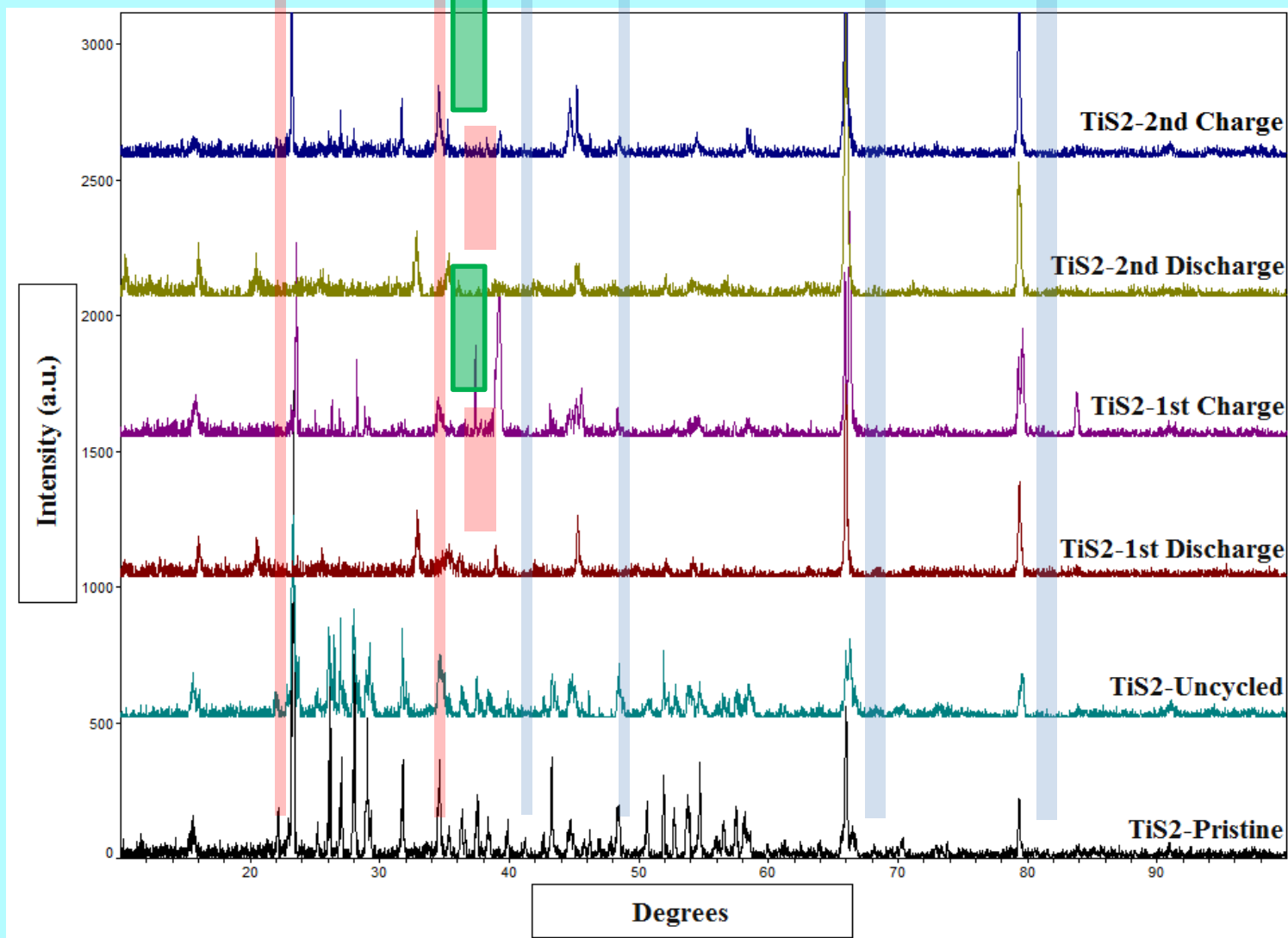


- Good performance considering the high cathode loading and high proportion of sulfur (4.6 mAh/cm<sup>2</sup> per side)
- High coulombic efficiency suggests polysulfide trapping.

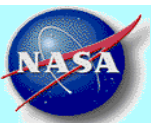




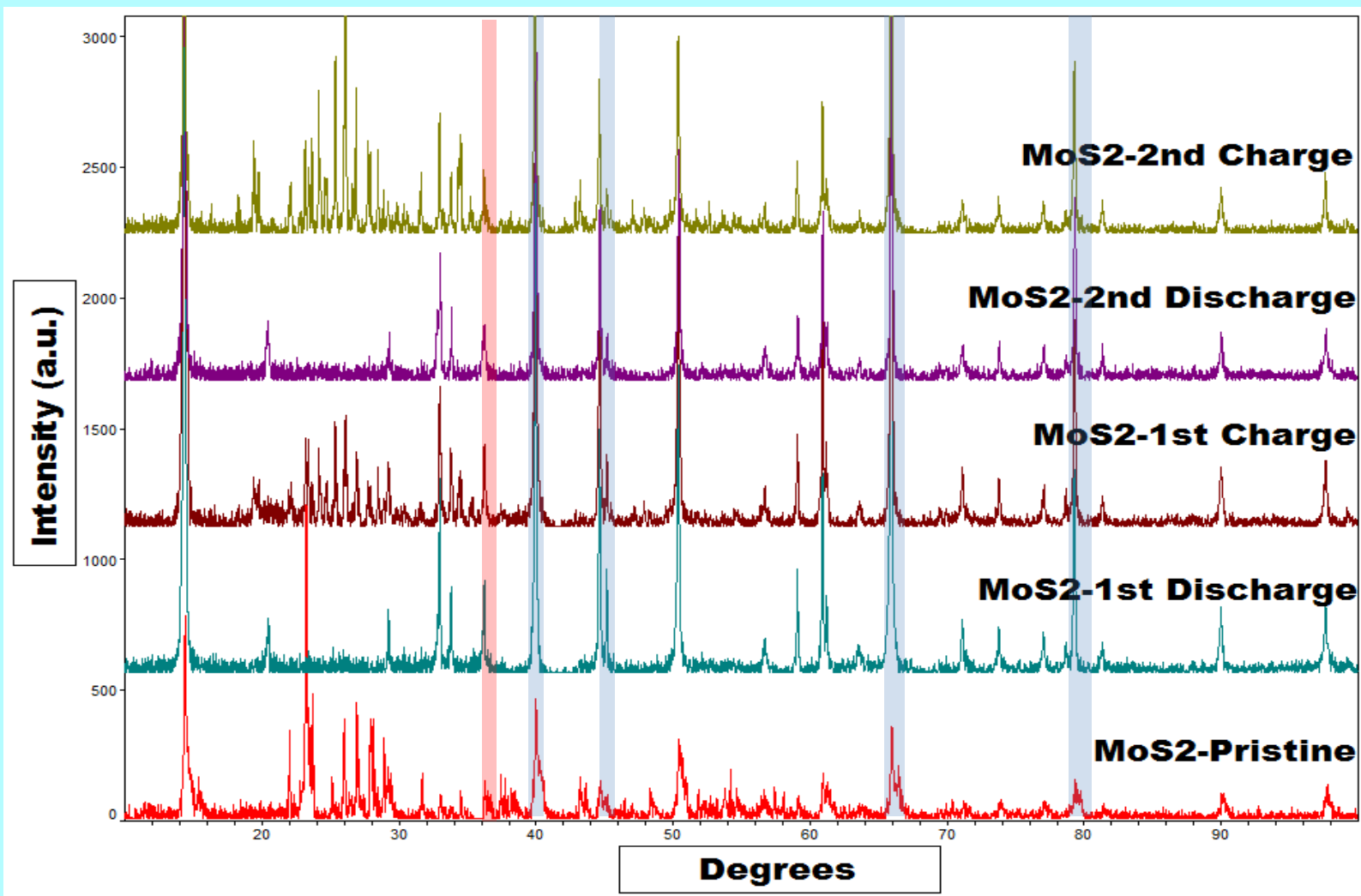
# X-ray Diffraction (XRD): $\text{TiS}_2$ - Blended Sulfur Cathode



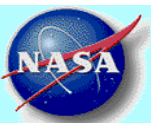
- Blue shades ~ Al foil contribution; Red Shades ~  $\text{LiTiS}_2$ ; Green shades ~  $\text{TiS}_2$
- The XRD spectra for  $\text{TiS}_2$  electrodes showed a transition from  $\text{TiS}_2$  to  $\text{LiTiS}_2$  after discharge and transition from  $\text{LiTiS}_2$  to  $\text{TiS}_2$  after charge.



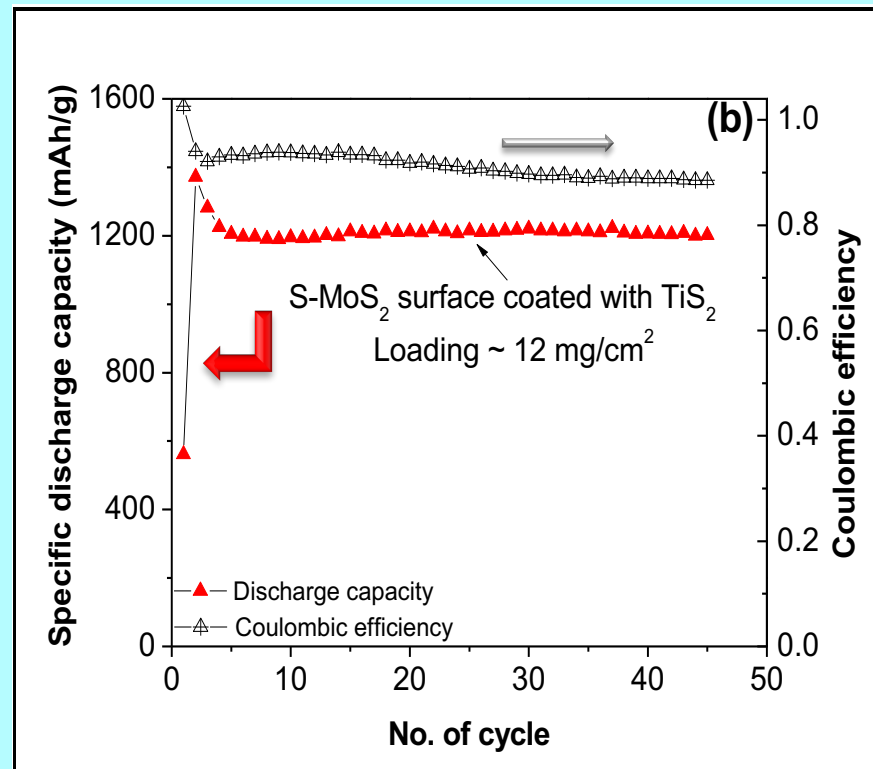
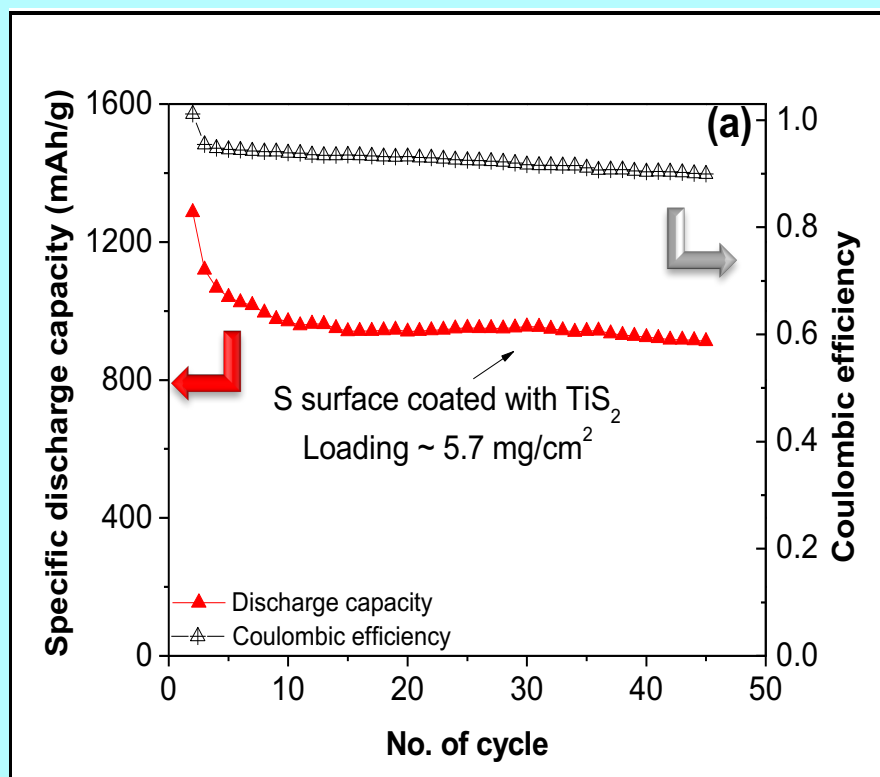
# X-ray Diffraction (XRD): MoS<sub>2</sub>- Blended Sulfur Cathode



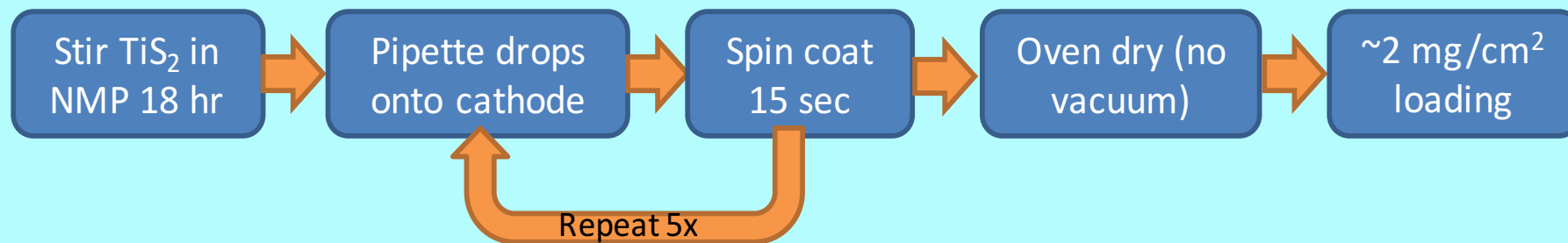
- Blue shades ~ Al foil contribution; Red Shades ~ MoS<sub>2</sub>.
- Similar to the baseline and MoS<sub>2</sub> electrodes the S-MoS<sub>2</sub> cathode showed the presence of sulfur peaks after charging and disappearance of the same peaks after discharging.
- No change in the MoS<sub>2</sub> peaks

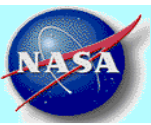


# Metal Sulfide Coating as Polysulfide Blocking Layer



- Cycling performance of a conventional sulfur improves with a coating of  $\text{TiS}_2$ .
- The sulfur cathode blended with  $\text{MoS}_2$  and coated with  $\text{TiS}_2$  shows a high specific capacity ( $\sim 1200 \text{ mAh/g}$ ) relative to S and good cycling stability even with an overall material loading of  $\sim 13 \text{ mg/cm}^2$ . A portion of this capacity is contributed by  $\text{TiS}_2$ .



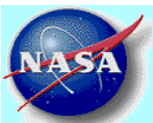


## Physical and Chemical Entrapment with $\text{TiS}_2$

### Cui's ab initio simulations

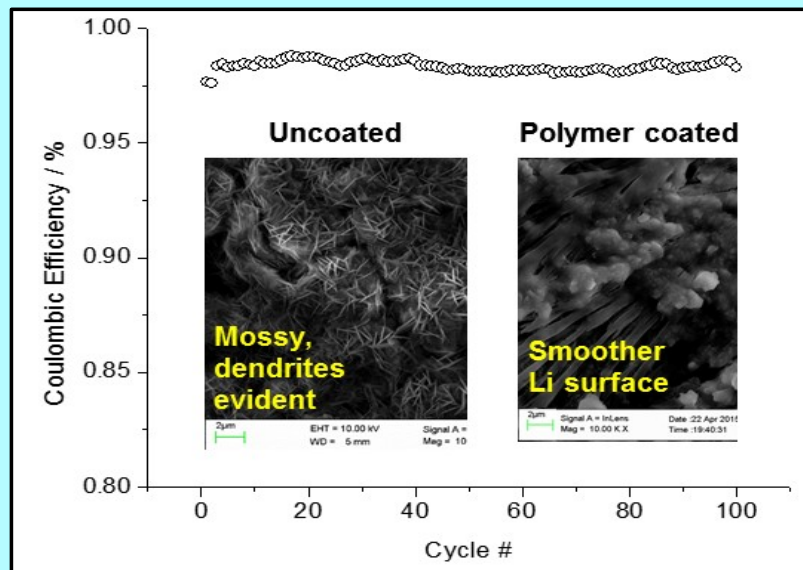
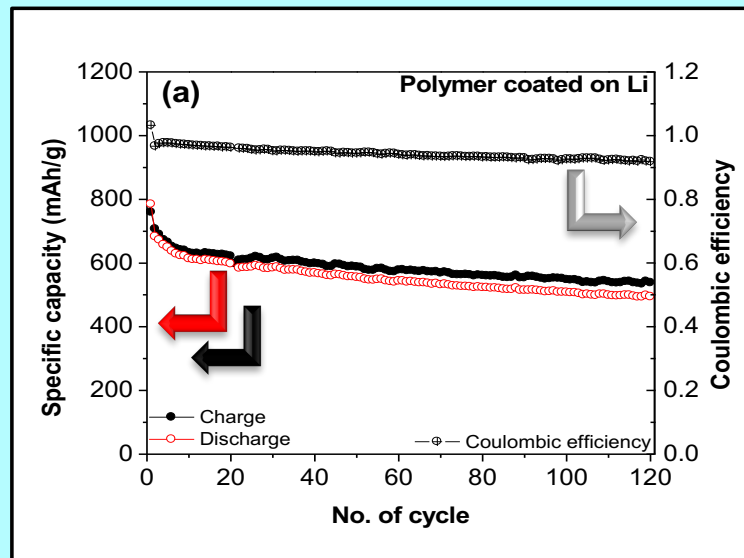
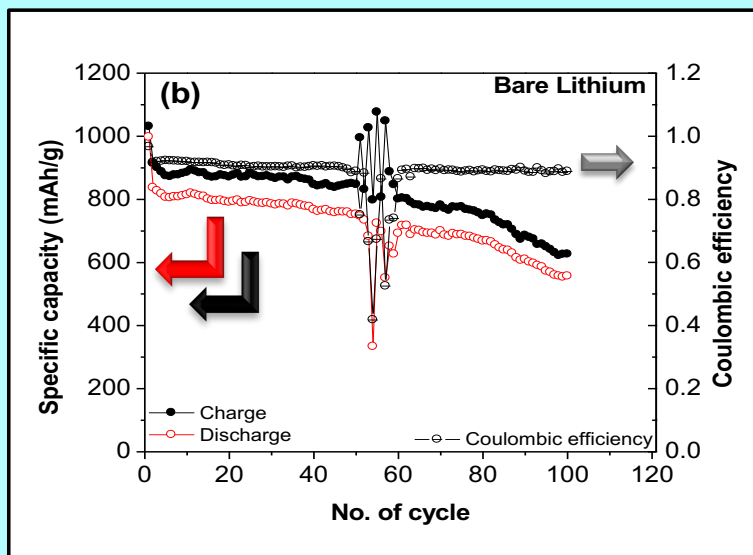
- Strong Li–S interaction (between the Li atoms in  $\text{Li}_2\text{S}$  and S atoms in  $\text{TiS}_2$ ), as well as strong S–S interaction between the S atoms in  $\text{Li}_2\text{S}$  and S atoms in  $\text{TiS}_2$ ).
- The binding energy between  $\text{Li}_2\text{S}$  and a single layer of  $\text{TiS}_2$  was calculated to be 2.99 eV. This value is 10 times higher than that between  $\text{Li}_2\text{S}$  and a single layer of carbon-based graphene, which is a very common encapsulation material used.
- The much stronger interaction between  $\text{Li}_2\text{S}$  and  $\text{TiS}_2$  can be explained by their similar ionic bonding and polar nature, unlike graphene which is covalently bonded and nonpolar in nature.
- Entities that bind strongly to  $\text{Li}_2\text{S}$  exhibit strong binding with  $\text{Li}_2\text{S}_n$  species as well owing to their similar chemical bonding nature.

Cui et al: Nature material Nature Communications 2014 | 5:5017 | DOI: 10.1038



# Polymer coating on a metal sulfide –blended cathode

3 layers of PEDOT-PEO Polymer spin coated on S:TiS<sub>2</sub>:CB:PVDF(65:15:15:5)

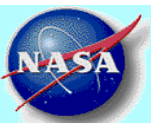


Cathode loading: 9 mg/cm<sup>2</sup>

Half-cell

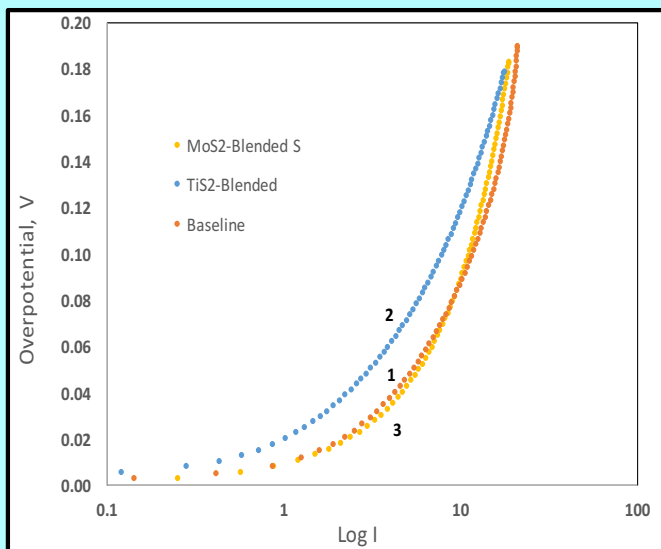
- Stable capacity with the PE-coated cathode, but slightly lower capacity than bare Li.





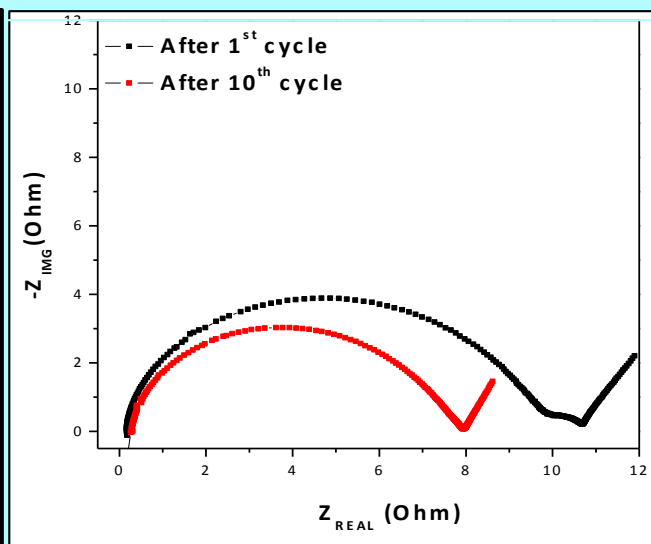
# Kinetics of Sulfur Cathode

## Kinetics Tafel Polarization



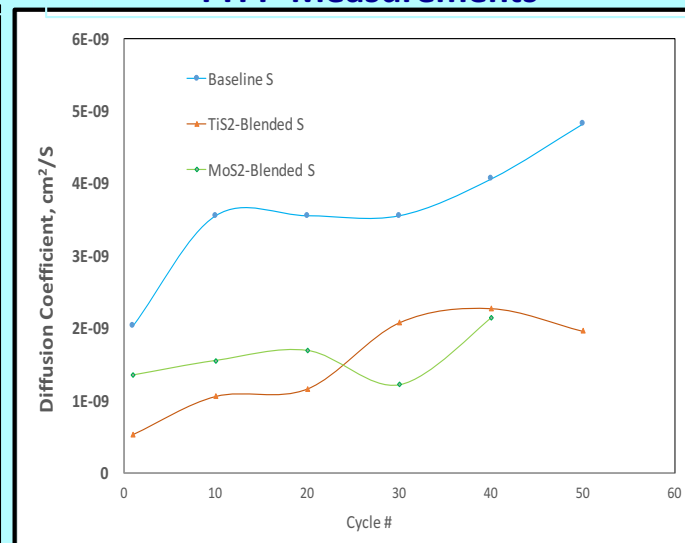
- Identical kinetics for sulfur reduction
- The exchange current density of pristine sulfur cathode is 0.19 mA/cm<sup>2</sup>. In contrast, the exchange current densities of the composite cathodes with TiS<sub>2</sub> and MoS<sub>2</sub> blends are 0.21 mA/cm<sup>2</sup> and 0.23 mA/cm<sup>2</sup>, respectively

## EIS of MoS<sub>2</sub>-Blended S Cathode

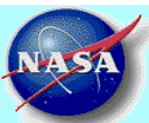


- Stable interface and lower impedance upon cycling

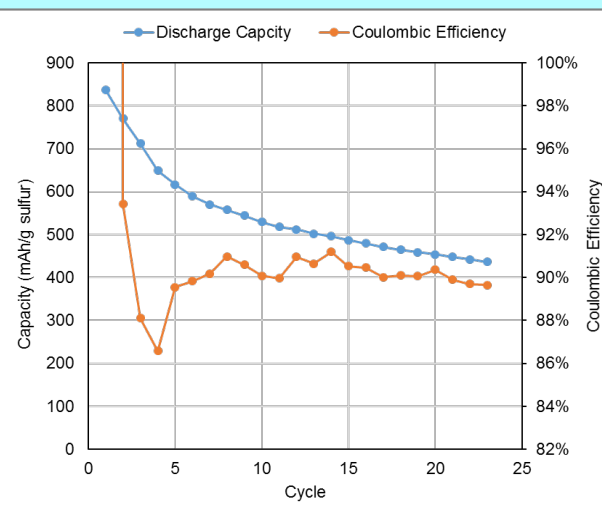
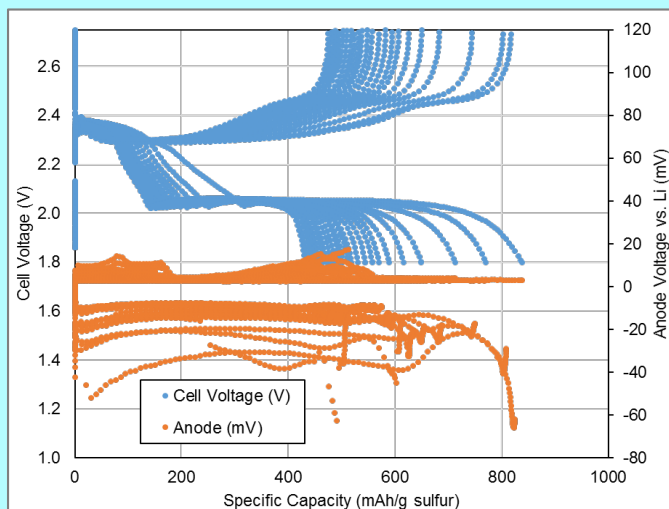
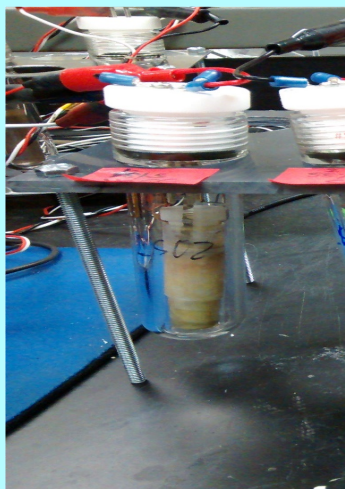
## Diffusional Kinetics from PITT Measurements



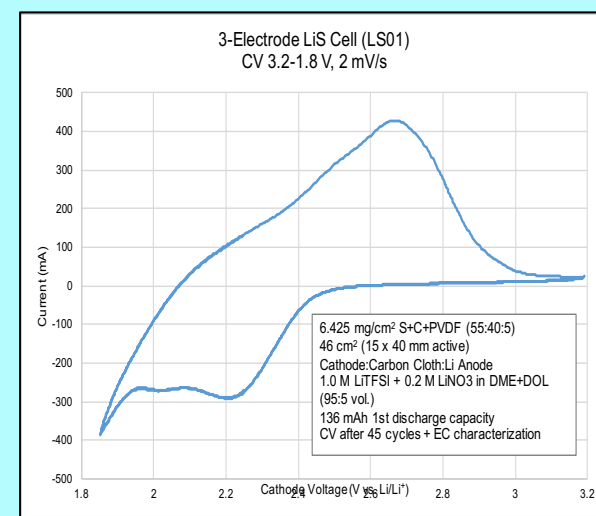
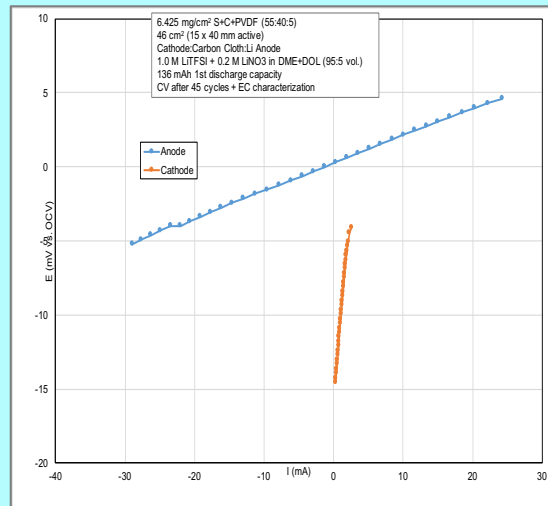
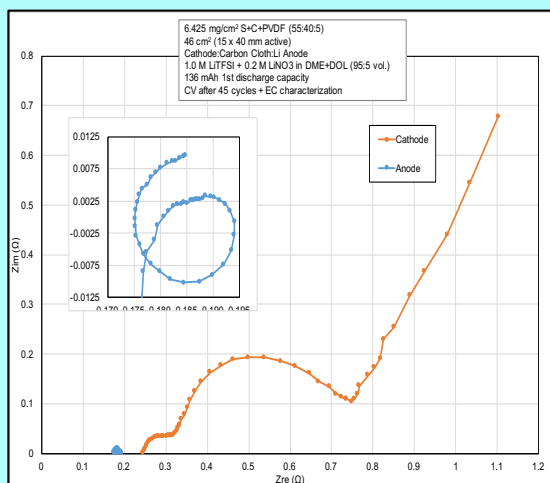
- Similar kinetics for Li diffusion in the cathodes.



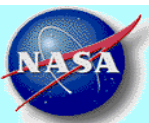
# Three-Electrode Li-S cells



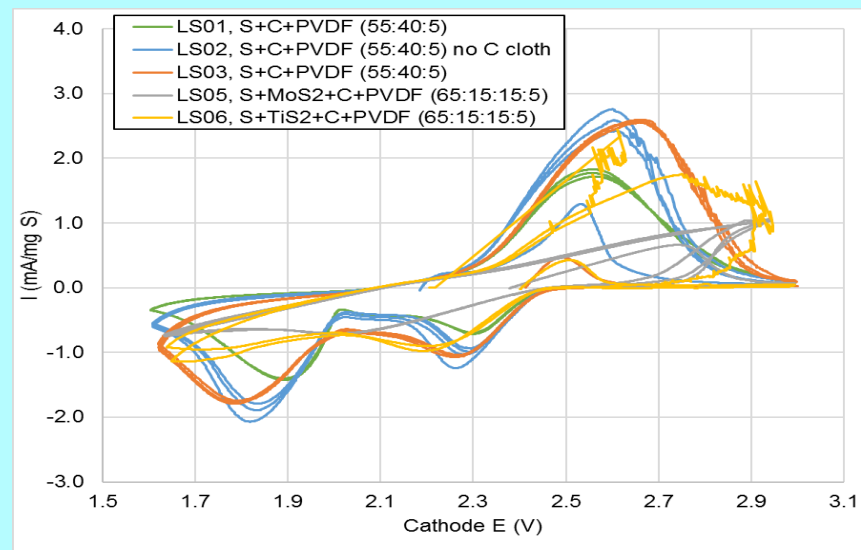
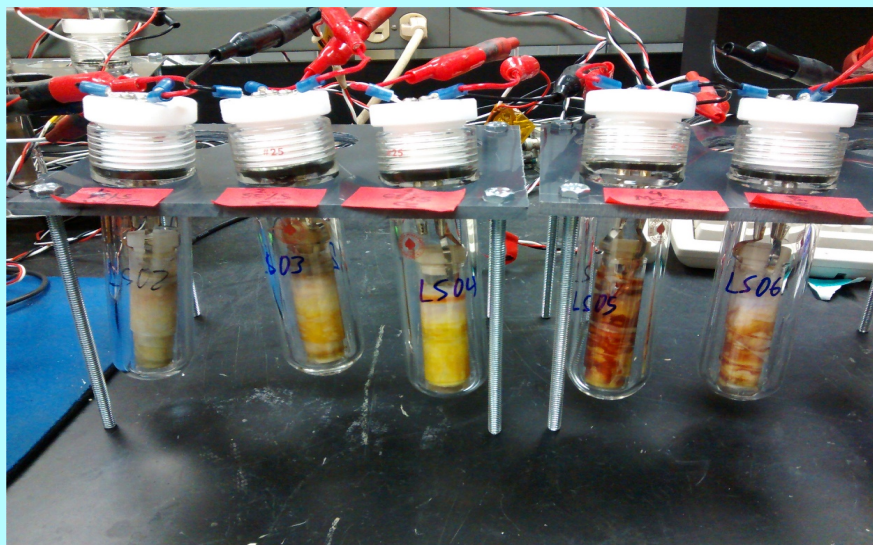
- Performance similar to that in coin cells. Lithium over potentials are insignificant



- Electrolyte color changes during cycling

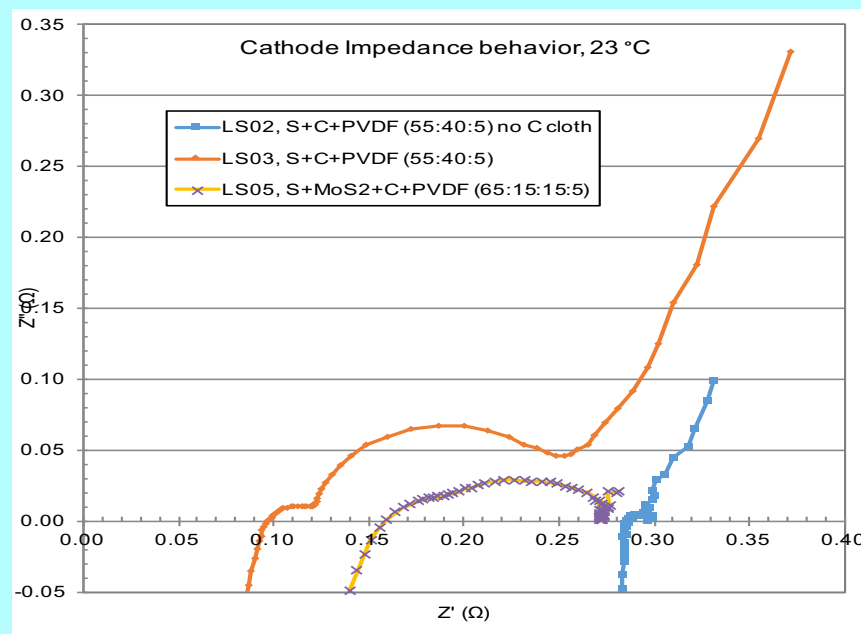


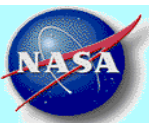
# Li-S wound 3-electrode cells with baseline S and S-blended with MoS<sub>2</sub> or TiS<sub>2</sub>



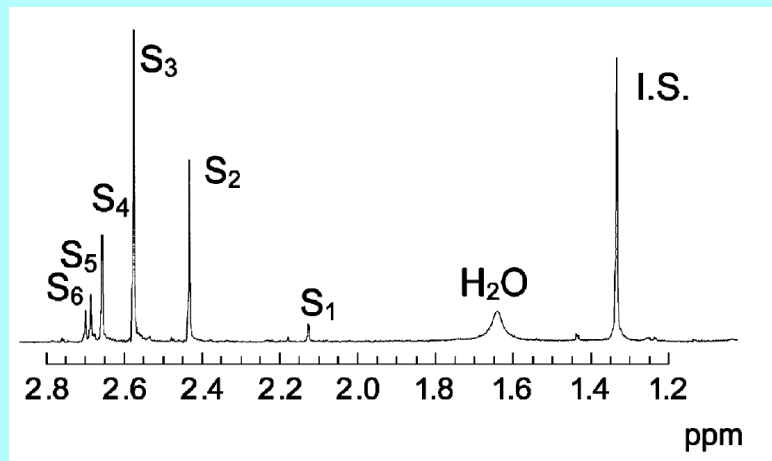
- Electrolyte color changes during cycling

| Cell ID | Sample     | Loading (mg/cm <sup>2</sup> ) | Theoretical Capacity (mAh) |
|---------|------------|-------------------------------|----------------------------|
| LS02    | 0214-S55-1 | 5.3                           | 150.7                      |
| LS03    | 0214-S55-2 | 5.5                           | 157.6                      |
| LS04    | 0214-S65-3 | 6.6                           | 222.2                      |
| LS05    | 0214-Mo-4  | 10.3                          | 348.9                      |
| LS06    | 0214-Ti-5  | 9.5                           | 322.3                      |

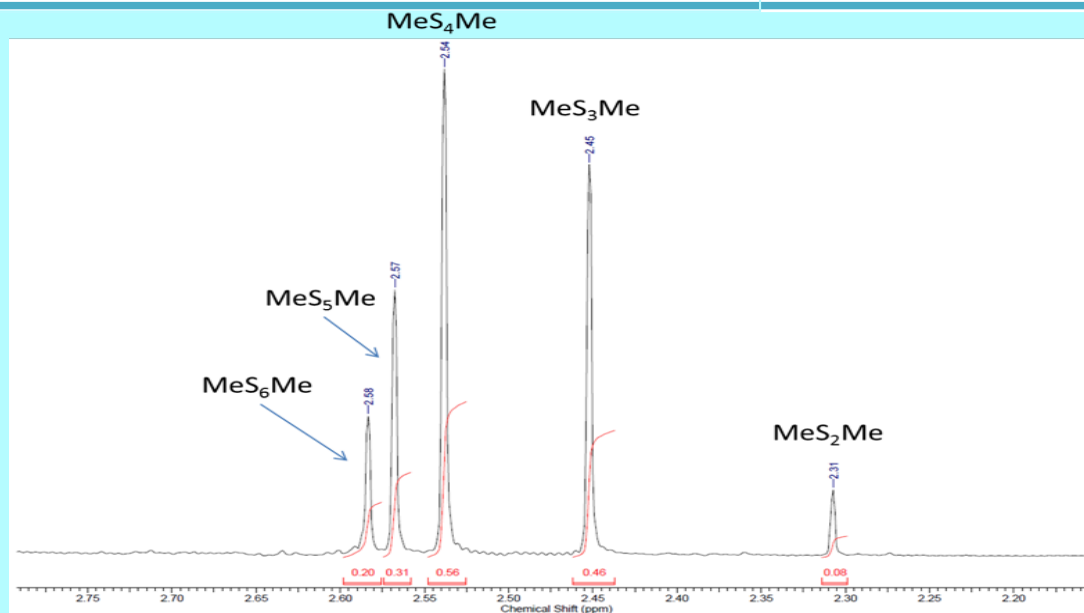




# Polysulfides in Electrolytes



$^1\text{H}$  NMR spectrum from methylated polysulfide solution (D. S. Argyropoulos, Y. Hou, R. Ganesaratnam, D. N. Harpp, and K. Koda, *Holzforschung*, 59, 124–131 (2005)).



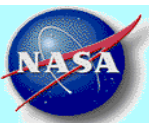
$^1\text{H}$  NMR spectrum from Li-S Ti cell (after 10 cycles)

- Cycle pouch cell 10 times
- Remove electrolyte with syringe (~1.5 mL)
- Add 0.1 mL dimethyl sulfate and stir at rt
- Add 1 mL  $\text{CDCl}_3$
- Acquire  $^1\text{H}$  NMR

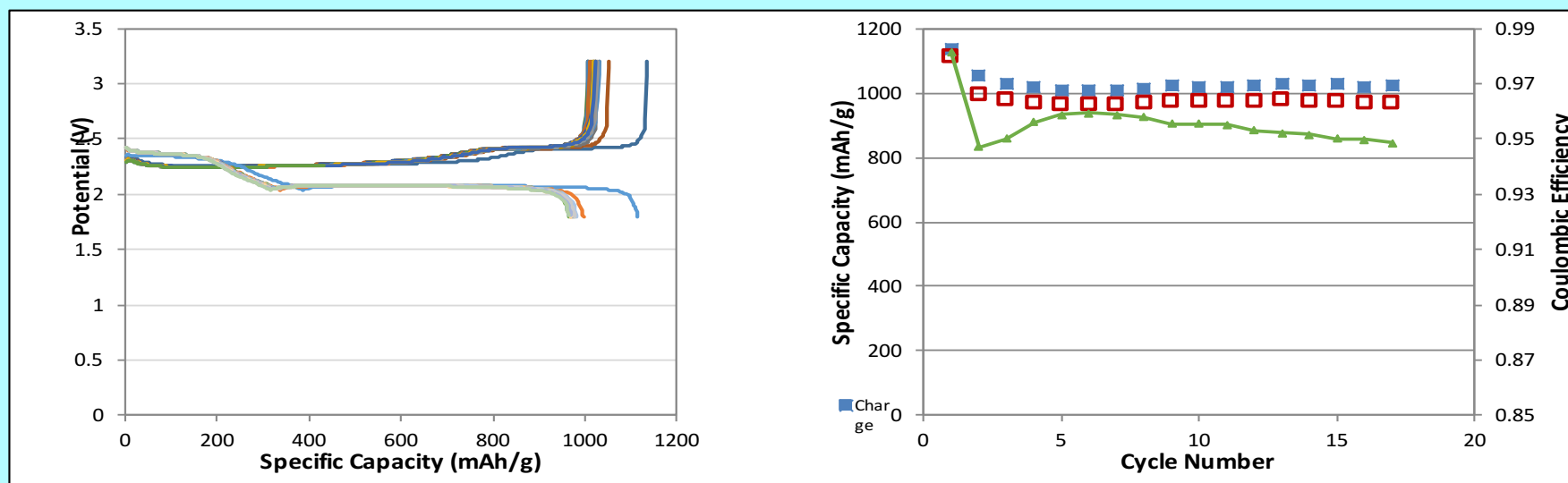
The total content of polysulfides was found to be 4.65 % in the Li/S-MoS<sub>2</sub> cell and 2.97 % in Li/S-TiS<sub>2</sub> cell.

|                | LiS-Mo | LiS-Ti |
|----------------|--------|--------|
| S <sub>2</sub> | 0.21 % | 0.09 % |
| S <sub>3</sub> | 1.39 % | 0.68 % |
| S <sub>4</sub> | 1.61 % | 1.18 % |
| S <sub>5</sub> | 0.90 % | 0.57 % |
| S <sub>6</sub> | 0.54 % | 0.45 % |
| Total          | 4.65 % | 2.97 % |

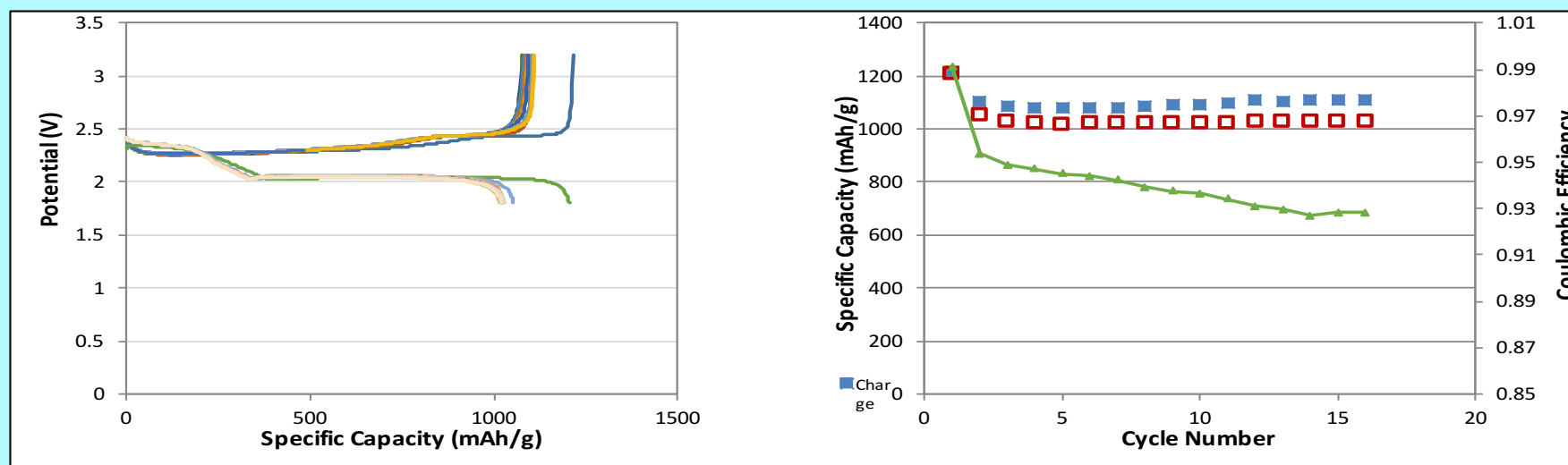
Polysulfides in electrolyte



# Li-S cells with New Separators



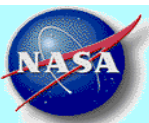
**Composition: (55:40:5) Loading: 6.25mg/cm<sup>2</sup>; Second discharge capacity 997.15mAh/g**



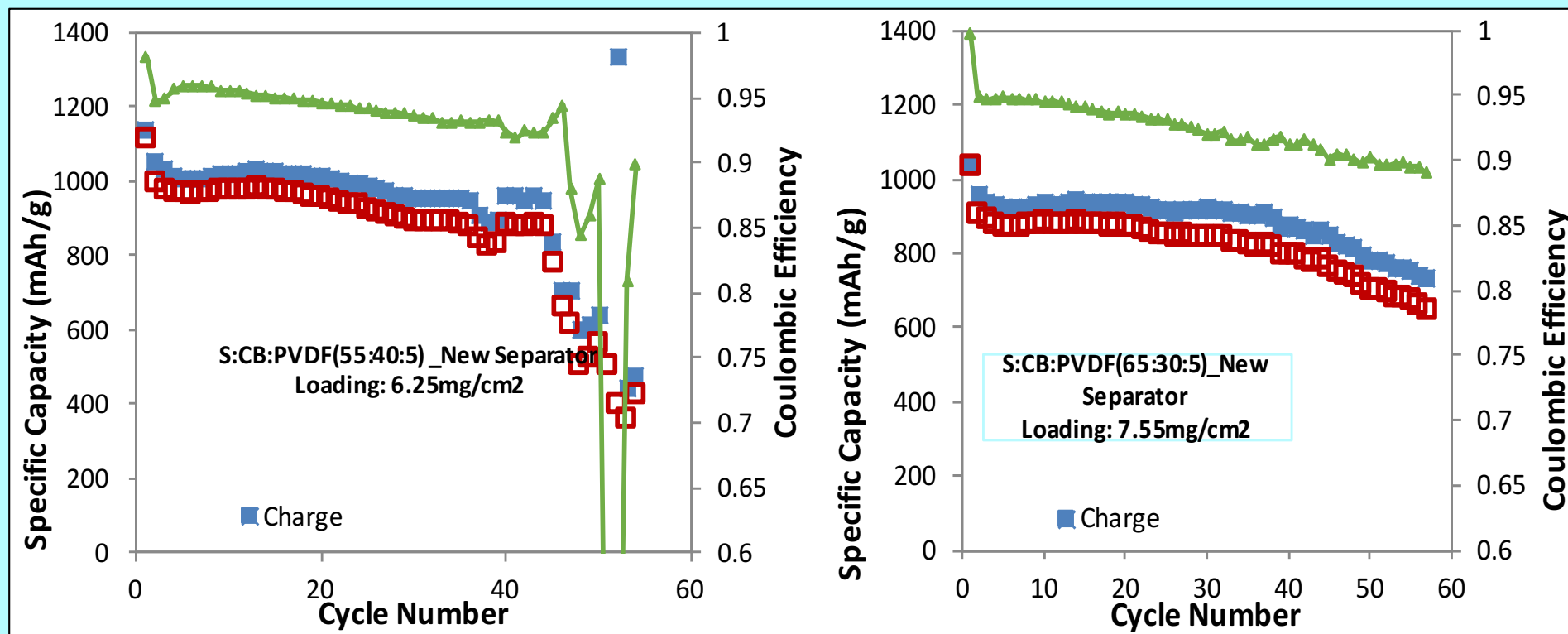
**S:CB:PVDF(65:30:5)\_Cloth New Separator\_1mm Spacer  
Loading: 8.1mg/cm<sup>2</sup> 2-nd Disch.Cap. 1052.76mAh/g**

**(Composition: 65:30:5) Loading: 8.1mg/cm<sup>2</sup>; 2-nd Discharge Capacity: 997.15mAh/g**

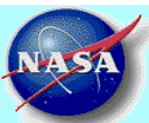




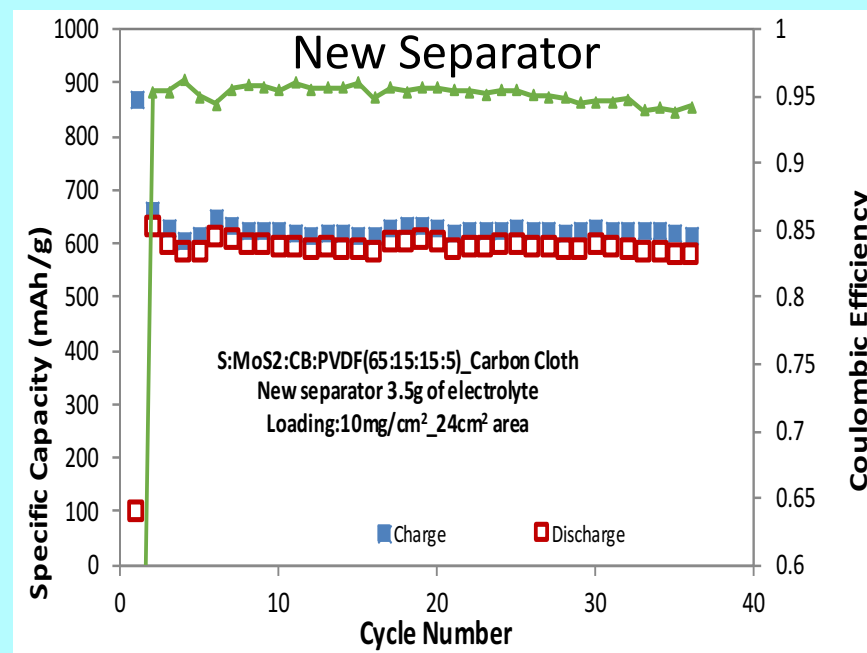
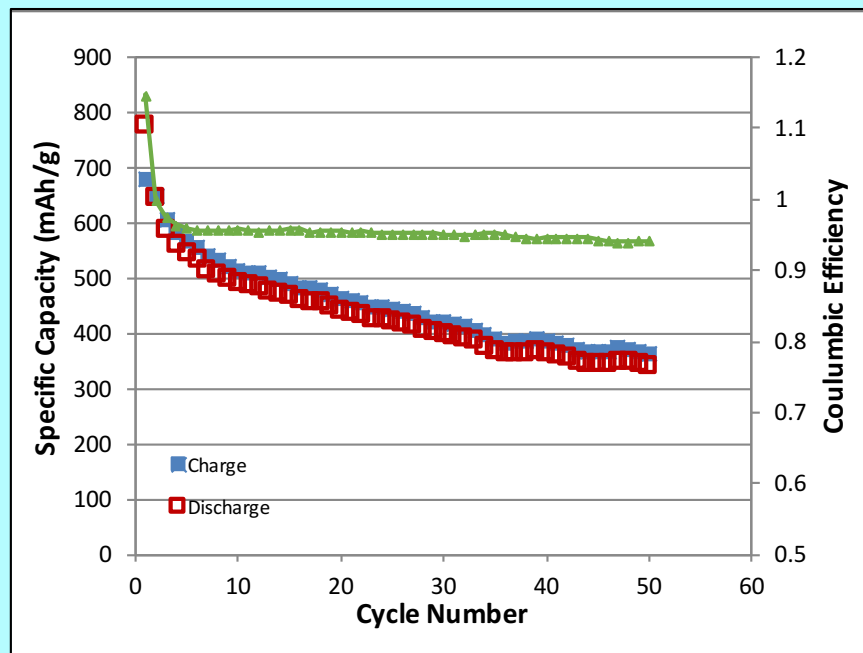
## Performance Li-S cells with the new separator



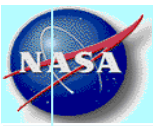
- Failure around 50 cycles due to anode. Requires anode protection



# Li- S Pouch Cells

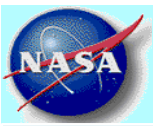


- Fabrication of Li-S pouch cells is tricky (amount of electrolyte).
- Good coulombic efficiency but a high fade rate during cycling (baseline sulfur)
- Excellent performance with high sulfur content (65%) and loading (10 mg/cm<sup>2</sup>) with MoS<sub>2</sub> blending (15%) and new separator



# Summary

- Novel sulfur/metal sulfide ( $\text{TiS}_2$  and  $\text{MoS}_2$ ) and sulfur composite cathodes display high capacity of  $\geq 800 \text{ mAh/g}$  (based on sulfur content), high coulombic efficiency and good cycle life ( $>75\%$  retention through 80 cycles of 100% depth of discharge) at C/3 rate.
  - High cathode loadings ( $12 \text{ mg/cm}^2$  or  $\sim 6 \text{ mAh/cm}^2$  per side) were demonstrated in Li-S cells containing composite cathodes with good utilization
  - Result in a high specific energy of  $400 \text{ Wh/kg}$  in prototype cells.
- In addition to the metal sulfide blends, metal sulfide coatings also improve the cycle life by minimizing the polysulfides in the electrolyte.
- PEDOT-co-PEO polymer-coating of Li anode provides some protection from polysulfides in full Li-S cells and improves cycle life. Ceramic electrolyte protected Li anodes are under evaluation.
- New separators and metal sulfide blends/coatings offer interesting opportunities for further advances in this technology.



# Acknowledgements

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